



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C04B 24/14	A2	(11) International Publication Number: WO 99/48833 (43) International Publication Date: 30 September 1999 (30.09.99)		
<table style="width: 100%; border: none;"> <tr> <td style="width: 50%; vertical-align: top; padding: 5px;"> (21) International Application Number: PCT/GB99/00926 (22) International Filing Date: 24 March 1999 (24.03.99) (30) Priority Data: <div style="display: flex; justify-content: space-between; margin-top: 5px;"> <div>9806314.2</div> <div>24 March 1998 (24.03.98)</div> <div>GB</div> </div> <div style="display: flex; justify-content: space-between; margin-top: 5px;"> <div>9812929.9</div> <div>15 June 1998 (15.06.98)</div> <div>GB</div> </div> <div style="display: flex; justify-content: space-between; margin-top: 5px;"> <div>9821152.7</div> <div>29 September 1998 (29.09.98)</div> <div>GB</div> </div> (71) Applicant (for all designated States except US): BPB PLC [GB/GB]; Langley Park House, Uxbridge, Slough SL3 6DU (GB). (72) Inventors; and (75) Inventors/Applicants (for US only): O'KEEFE, Samantha, Jane [GB/GB]; 36 Barton Road, Barlestone, Nuneaton, Warks CV13 0EP (GB). FREEGARD, Graham, John [GB/GB]; 3 The Mews, Colston Bassett, Notts NG12 3FB (GB). (74) Agent: MARLOW, Nicholas, Simon; Reddie & Grose, 16 Theobalds Road, London WC1X 8PL (GB). </td> <td style="width: 50%; vertical-align: top; padding: 5px;"> (81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>Without international search report and to be republished upon receipt of that report.</i> </td> </tr> </table>			(21) International Application Number: PCT/GB99/00926 (22) International Filing Date: 24 March 1999 (24.03.99) (30) Priority Data: <div style="display: flex; justify-content: space-between; margin-top: 5px;"> <div>9806314.2</div> <div>24 March 1998 (24.03.98)</div> <div>GB</div> </div> <div style="display: flex; justify-content: space-between; margin-top: 5px;"> <div>9812929.9</div> <div>15 June 1998 (15.06.98)</div> <div>GB</div> </div> <div style="display: flex; justify-content: space-between; margin-top: 5px;"> <div>9821152.7</div> <div>29 September 1998 (29.09.98)</div> <div>GB</div> </div> (71) Applicant (for all designated States except US): BPB PLC [GB/GB]; Langley Park House, Uxbridge, Slough SL3 6DU (GB). (72) Inventors; and (75) Inventors/Applicants (for US only): O'KEEFE, Samantha, Jane [GB/GB]; 36 Barton Road, Barlestone, Nuneaton, Warks CV13 0EP (GB). FREEGARD, Graham, John [GB/GB]; 3 The Mews, Colston Bassett, Notts NG12 3FB (GB). (74) Agent: MARLOW, Nicholas, Simon; Reddie & Grose, 16 Theobalds Road, London WC1X 8PL (GB).	(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>Without international search report and to be republished upon receipt of that report.</i>
(21) International Application Number: PCT/GB99/00926 (22) International Filing Date: 24 March 1999 (24.03.99) (30) Priority Data: <div style="display: flex; justify-content: space-between; margin-top: 5px;"> <div>9806314.2</div> <div>24 March 1998 (24.03.98)</div> <div>GB</div> </div> <div style="display: flex; justify-content: space-between; margin-top: 5px;"> <div>9812929.9</div> <div>15 June 1998 (15.06.98)</div> <div>GB</div> </div> <div style="display: flex; justify-content: space-between; margin-top: 5px;"> <div>9821152.7</div> <div>29 September 1998 (29.09.98)</div> <div>GB</div> </div> (71) Applicant (for all designated States except US): BPB PLC [GB/GB]; Langley Park House, Uxbridge, Slough SL3 6DU (GB). (72) Inventors; and (75) Inventors/Applicants (for US only): O'KEEFE, Samantha, Jane [GB/GB]; 36 Barton Road, Barlestone, Nuneaton, Warks CV13 0EP (GB). FREEGARD, Graham, John [GB/GB]; 3 The Mews, Colston Bassett, Notts NG12 3FB (GB). (74) Agent: MARLOW, Nicholas, Simon; Reddie & Grose, 16 Theobalds Road, London WC1X 8PL (GB).	(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>Without international search report and to be republished upon receipt of that report.</i>			
(54) Title: GYPSUM COMPOSITION				
$ \left[\text{CH}_2 - \overset{\text{OCH}_3}{\underset{\text{O}=\text{C} \quad \text{O}=\text{C}}{\text{CH}}} - \text{CH} - \text{CH} \right] \quad (\text{III}) $				
(57) Abstract <p>The invention provides ready mixed gypsum plaster jointing compounds with long shelf lives which can be induced to set by the addition of an accelerator. In a first aspect, the invention provides ready mixed composition comprising: calcium sulphate hemihydrate; water; and a retarder comprising a polymer or a copolymer of a monomer of formula (I) where x and y are integers and may be the same or different or an ionised form thereof. In a second aspect of the invention the retarder comprises a modified maleic anhydride polymer or copolymer. In a third aspect of the invention the retarder comprises a polymer or copolymer of a monomer having formula (II) wherein R is C₄H₉ or (CH₃)₂CH. In a fourth aspect of the invention the retarder comprises 0.09 to 0.1 % by weight plaster of a polymer or copolymer of a monomer having formula (III) and having a molecular weight in the range of about 110 000 to about 140 000. The invention also provides a ready mixed coating system comprising a gypsum composition as described above and a setting accelerator which when mixed with the cementitious composition induces the cementitious composition to set.</p>				

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

GYPSUM COMPOSITION

The present invention relates to a cementitious composition which is relatively stable when mixed with water and which
5 can be induced to set and harden when an accelerator is mixed into the composition. Such compositions are useful in a variety of applications, including as joint compounds for finishing joints between adjacent gypsum wallboards.

Interior walls are commonly constructed using gypsum
10 plasterboard panels. An interior wall is made by securing the plasterboard to a support structure. The joints between the wallboard panels are then concealed using a joint compound. Typically, a wetted joint compound is embedded in the joint together with a paper reinforcing tape and the
15 joint compound is then allowed to dry. After the joint compound has dried, a second coat of joint compound is applied, left to dry, and if necessary sanded before the wall is finished with a conventional decorative coating.

Conventional joint compounds are supplied in the form
20 of a dry powder which is mixed with water at the work site before application to the joint or as ready mixed joint compounds which are pre-mixed with water during manufacture. Such ready mixed formulations have the advantage that they are of consistent composition, do not require water at the
25 work site and do not take time to prepare.

Two types of joint compounds are known: drying type joint compounds and setting type joint compounds. The drying type comprise a filler, predominantly of calcium carbonate, a binder, a thickener, and other standard
30 ingredients. These components are mixed with water prior to use and are then left to dry after application. Drying type joint compounds have the disadvantage that they are prone to shrinkage as they dry. Such shrinkage makes a level wall surface hard to achieve. Further, each coat of drying type
35 compound must be left to dry before a subsequent coat is applied. If a coat of drying type compound is applied to an earlier coat which has not completely dried, the subsequent

- 2 -

coat may be ruined as the previous coat shrinks underneath it.

The setting type of joint compounds comprise an inorganic binder predominantly calcium sulphate hemihydrate (calcined gypsum), a filler, an organic binder and a thickener, usually together with other standard ingredients. Conversion of the calcium sulphate hemihydrate to calcium sulphate dihydrate causes the joint compound to harden and set. This hydration takes place over a relatively short period of time. Consequently, the setting type of joint compounds are sold in powder form so that they do not set in the packaging before they can be applied to the joint. The setting type of joint compounds set and harden faster than the drying type of joint compound and are less prone to shrinkage.

Because of the advantages of setting type joint compounds over drying type joint compounds and because of the advantages of ready mixed formulations, several attempts have been made to produce setting type ready mixed joint compound formulations which have a long shelf life, which have good workability after the accelerator is added until hardening takes place, which are not prone to shrinkage and which set and harden over a short time so that the time necessary between application of successive coats is reduced.

US-A-4 661 161 describes setting type ready mixed joint compounds comprising calcium sulphate hemihydrate, a retarder comprising a proteinaceous agent and a calcium ion chelating agent and other conventional joint compound ingredients. Setting is induced with an aqueous solution of compounds having ions which have a higher log K value than calcium, such as compounds of ferric or ferrous ions or compounds of aluminium ions. Such compositions are found to have setting times which can be controlled depending on the amount of accelerator added and are disclosed to have an adequately long shelf life for commercialisation. However, it has been found that as joint compounds of this type age,

- 3 -

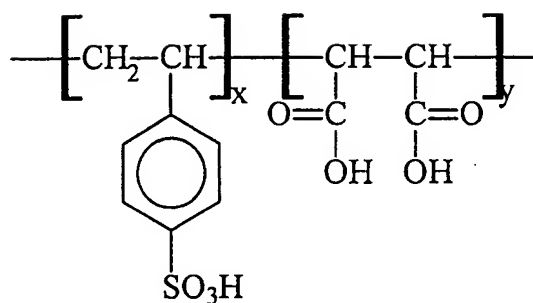
they require less accelerator to achieve the same setting time, making their use unpredictable and uncontrollable. Further, the shelf life has been found to be insufficiently long, such that the joint compound is observed to set in the packaging.

EP-A-0 681 998 discloses an improved setting type ready mixed joint compound which is retarded by a non calcium-bearing phosphate (for example sodium pyrophosphate, zinc hexametaphosphate, potassium tripolyphosphate). Setting is induced with compounds having ions which have a higher log K value than calcium. The preferred accelerator is zinc sulphate. Again, the setting time is controllable depending on the amount of accelerator added.

US-A-5 653 797 discloses a setting type ready mixed joint compound retarded by a copolymer of acrylic acid and acrylamide, or a blend of the two homopolymers. Setting is accelerated using metallic salts that provide acidic cations such as aluminium, potassium, calcium or ferric sulphate, or ferric chloride. The setting time is controllable depending on the amount of accelerator added.

Many setting type ready mixed joint compounds have not been found to be commercially viable because of their relatively short shelf lives. It is desirable therefore to produce an alternative setting type ready mixed joint compound which has a longer shelf life and which has short setting times after activation with an accelerator, good workability after the accelerator is added until setting and hardening take place and good shrinkage properties.

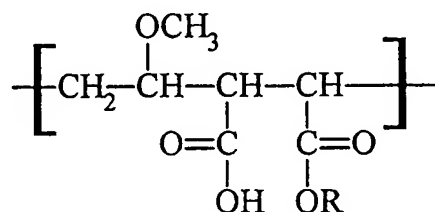
According to a first aspect of the invention there is provided a ready mixed cementitious composition which sets when mixed with an effective amount of a setting accelerator comprising a mixture of: a cementitious material; water; and a retarder comprising a polymer or a copolymer of a monomer of the formula:



where x and y are integers and may be the same or different or a metal salt or an ionised form thereof.

According to a second aspect of the invention there is provided a ready mixed cementitious composition which sets when mixed with an effective amount of a setting accelerator comprising a mixture of: a cementitious material; water; and a retarder comprising a rosin modified maleic anhydride polymer or copolymer where x and y are integers and may be the same or different or an ionised form thereof.

10 According to a third aspect of the invention there is provided a ready mixed cementitious composition which sets when mixed with an effective amount of a setting accelerator, the composition comprising a mixture of: a cementitious material; water; and a retarder comprising a
15 polymer or copolymer of a monomer having the formula:

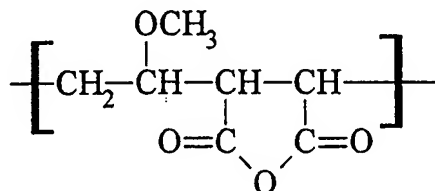


wherein R is C_4H_9 or $(CH_3)_2CH$ where x and y are integers and may be the same or different or an ionised form thereof.

According to a fourth aspect of the invention there is
20 provided a ready mixed cementitious composition which sets
when mixed with an effective amount of a setting
accelerator, the composition comprising:

- 5 -

a calcium sulphate hemihydrate; water; and a retarder comprising 0.09 to 0.1% by weight plaster of a polymer or copolymer of a monomer having the formula:



5 and having a molecular weight in the range of about 110 000 to about 140 000 where x and y are integers and may be the same or different or an ionised form thereof.

Preferably the cementitious material is a calcium sulphate hemihydrate, most preferably alpha calcium sulphate hemihydrate. Also preferably the polymer retarder is
 10 dissolved in isopropyl alcohol. Also preferably, the pH of the composition is at least 7.

The polymer is preferably present in the composition in an amount of about 0.5% to about 5% by weight of calcium sulphate hemihydrate in the composition. More preferably
 15 the polymer is present in the composition in an amount of about 1.4% by weight of calcium sulphate hemihydrate in the composition.

Preferred polymers for compositions according to the third aspect of the invention include Gantrez ES hydrolysed in isopropyl alcohol. A preferred source of the polymer of compositions according to the fourth aspect of the invention is Gantrez AN-119. Preferred polymers for compositions according to the second aspect of the invention include
 20 Ennesin FM-6 in isopropyl alcohol. Preferred polymers for compositions according to the first aspect of the invention include Narlex D72, a polymer of molecular weight about 15000. Calcium sulphate hemihydrate is preferably present in the composition in an amount of about 5% to about
 25 50% by weight of the composition. More preferably the calcium sulphate hemihydrate is present in the composition in an amount of about 30% by weight of the composition.

- 6 -

Compositions according to the third and fourth aspects of the invention can advantageously contain a small amount of an accelerator; insufficient to cause the composition to set but sufficient to thicken it. Preferred amounts of
5 accelerator to achieve thickening of the composition without setting are about 0.1% to 1%. Setting is achieved by addition of further accelerator.

Preferred compositions according to the invention further comprise at least one of a binder, a thickener and
10 a filler.

The binder may be any conventional polymeric binder such as an acrylic, styrene acrylic, styrene butadiene, vinyl acetate and ethylene vinyl acetate, but is preferably ethylene vinyl acetate, preferably dispersed in water. The
15 binder is preferably present in the composition in an amount of about 1% to about 10%, more preferably in an amount of about 1% to about 7% by weight of the composition. Most preferably the binder is present in the composition in an amount of about 4% by weight of the composition.

The thickener may be any conventional thickener for example cellulose ether, modified cellulose ether, starch, gum arabic, acrylic, urethane or polyvinyl alcohol, but is preferably cellulose ether. The thickener is preferably present in the composition in an amount of about 0.05% to
20 about 5% by weight of the composition. More preferably the thickener is present in an amount of about 0.3% by weight of the composition.

The filler may be any conventional filler, for example perlite, limestone, dolomite, celite, silica, talc,
30 vermiculite, glass microspheres, polymer microspheres, kaolin or wollastonite but is preferably at least one of perlite, limestone and celite, and is preferably present in an amount of about 10% to 20% by weight of the composition. When limestone is used as a filler it is preferred that it is mixed with at least one other of the preferred fillers.
35 When perlite is used as a filler it is preferred that it is not added to the composition in excess of 12% by weight of

- 7 -

the solid components of the composition. When limestone is present in the composition it is preferred that the amount of limestone in the composition is from about 10% to about 20% by weight of the composition. Other conventional joint compound additives may be added to the composition. These include non levelling agents such as silicas and clays and preservatives such as formaldehyde and isothiazolones.

The invention also provides a ready mixed coating system comprising separate first and second components, the first component comprising a composition according to any of the first to fourth aspects of the invention and the second component comprising a setting accelerator which when mixed with the cementitious composition induces the cementitious composition to set.

The accelerator may be any conventional accelerator but preferably comprises at least one of aluminium sulphate, zinc sulphate or iron sulphate. More preferably the accelerator comprises aluminium sulphate. The accelerator may be added in the form of a powder, an aqueous solution, or a paste. The amount of accelerator added to stimulate the setting of compositions according to the invention is preferably about 1% to about 5% by weight of the composition. More preferably the amount of accelerator added is about 2% by weight of the composition.

Also according to the invention there is provided a method for preparing a setting coating composition comprising admixing first and second components of the composition, the first component comprising a ready mixed cementitious composition according to any of the first to fourth aspects of the invention, and the second component being a setting accelerator, such as those described above.

The mixing of the first component with the second component can be achieved in any conventional manner. The two components can be mixed together in bulk or they may simply be brought into contact with each other, for example by being separately coated onto a surface or by being separately coated onto respective surfaces which are then

- 8 -

brought together. If the system is used as a jointing compound, one component such as the accelerator can be applied to the tape. The other component is applied to the joint and the treated tape is placed on the filled joint.

5 The accelerator mixes with the first component at the interface between the components to bring about the setting of the first component. The first component can also be applied to a treated tape already in position over the joint.

10 The invention will be further described by way of example. Example 1 is according to the first aspect of the invention; Example 2 is according to the second aspect of the invention; Examples 3 to 12 are according to the third aspect of the invention and Example 13 is according to the first and the third aspects of the invention.

15

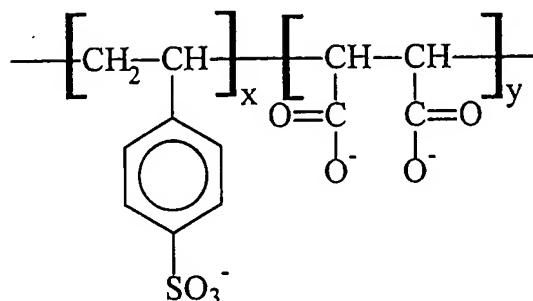
Example 1:

A ready mixed setting type joint compound was made with the following formulation:

		weight %
20	retarder	0.4
	cellulose ether	0.3
	lime	0.1
	calcium sulphate hemihydrate	29.6
	perlite	7.4
25	limestone	15.8
	wollastonite	2.6
	kaolin	2.6
	binder (ethylene vinyl acetate, 50% in water)	4.2
	water	37.0

- 9 -

The retarder was Narlex D72, the sodium salt of:



where x and y are integers and may be the same or different.

The retarder was pre-mixed with the lime and the water. The remaining components of the composition were mixed in
 5 using a high speed mixer to ensure that the mixture was homogeneous. A portion of this mixture was then removed for shelf life testing. 4% by weight of the composition of a 1.1 M solution of aluminium sulphate was then added to the remainder of the mixture to accelerate hardening and setting
 10 of the mixture. The accelerator was hand mixed or drill mixed into the composition.

The portion of the composition that was removed for shelf life testing had not set 3 months later.

Example 2:

15 A ready mixed setting type joint compound was made with the following formulation:

	weight %
retarder	0.8
cellulose ether	0.3
20 lime	1.0
calcium sulphate hemihydrate	28.7
perlite	7.2
limestone	16.4

- 10 -

	weight %
kaolin	5.1
attapulgate clay	0.5
binder (ethylene vinyl acetate, 50% in water)	4.1
water	35.9

5 The retarder was Ennesin FM-6.

The retarder as a 50% solution in isopropyl alcohol was pre-mixed with the lime and the water, then the remaining components of the composition were mixed in using a high speed mixer to ensure that the mixture was homogeneous. A
10 portion of this mixture was then removed for shelf life testing. 4% by weight of the composition of a 1.1 M solution of aluminium sulphate was then added to the remainder of the mixture to accelerate hardening and setting of the mixture. The accelerator was hand mixed or drill
15 mixed into the composition.

The portion of the composition that was removed for shelf life testing had not set 4 months later.

Example 3:

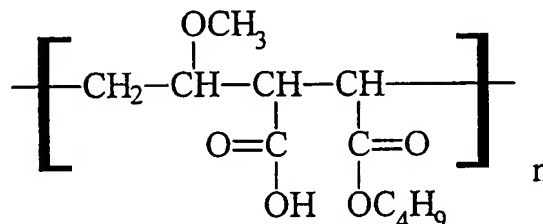
20 A ready mixed setting type joint compound was made according to the following formulation:

	weight %
retarder (50% in isopropyl alcohol)	0.8
cellulose ether	0.3
lime	1.0
calcium sulphate hemihydrate	29.2
25 perlite	7.3
limestone	15.6
celite	5.2

- 11 -

	weight %
binder (ethylene vinyl acetate, 50% in water)	4.2
water	36.4

The retarder was Gantrez ES-435, of the formula:



5 in isopropyl alcohol.

The retarder as a 50% solution in isopropyl alcohol was pre-mixed with the lime and the water, then the remaining components of the composition were mixed in using a high speed mixer to ensure that the mixture was homogeneous. The pH of the composition was 12.4. A portion of this mixture was then removed for shelf life testing. 4% by weight of the composition of a 1.1 M solution of aluminium sulphate was then added to the remainder of the mixture to accelerate hardening and setting of the mixture. The accelerator was hand mixed or drill mixed into the composition.

The portion of the composition that was removed for shelf life testing had not set ten months later. When the accelerator was hand mixed into the composition, the set time was 165 minutes. When the accelerator was drill mixed into the composition, the set time was 90 minutes. The composition was found to have excellent workability and surface properties, and when no accelerator was added to the ready mixed composition it was an excellent drying type joint compound.

- 12 -

Example 4:

A ready mixed setting type joint compound was made as in example 3 but with the following formulation:

		weight %
5	retarder (Gantrez ES-435, 50% in isopropyl alcohol)	0.8
	cellulose ether	0.3
	lime	0.1
	calcium sulphate hemihydrate	29.4
	perlite	7.4
10	limestone	15.8
	wollastonite	2.6
	kaolin	2.6
	binder (ethylene vinyl acetate, 50% in water)	4.2
	water	36.8

15 The portion of the composition that was removed for shelf life testing had not set 10 months later.

Example 5:

A ready mixed setting type joint compound was made as in example 3 but with the following formulation:

		weight %
20	retarder (Gantrez ES-435, 50% in isopropyl alcohol)	0.8
	cellulose ether	0.3
	lime	1.1
	calcium sulphate hemihydrate	30.4
25	perlite	7.6
	limestone	17.4

- 13 -

	weight %
wollastonite	2.7
kaolin	2.7
binder (ethylene vinyl acetate, 50% in water)	4.3
water	32.7
5 The portion of the composition that was removed for shelf life testing had not set 2½ months later.	

Example 6:

A ready mixed setting type joint compound was made as in example 6 but with the following formulation:

	weight %
10 retarder (Gantrez ES-435, 50% in isopropyl alcohol)	0.8
cellulose ether	0.3
lime	1.0
calcium sulphate hemihydrate	28.8
15 perlite	7.2
limestone	16.4
wollastonite	2.6
kaolin	2.6
attapulgate clay	0.3
20 binder (ethylene vinyl acetate, 50% in water)	4.1
water	35.9

The portion of the composition that was removed for shelf life testing had not set 7 months later.

- 14 -

Example 7:

A ready mixed setting type joint compound was made as in example 3 but with the following formulation:

		weight %
	retarder (Gantrez ES-435, 50% in isopropyl	0.7
5	alcohol)	
	cellulose ether	0.3
	lime	0.1
	calcium sulphate hemihydrate	28.1
	perlite	7.0
10	limestone	16.1
	wollastonite	2.5
	talc	2.5
	binder (ethylene vinyl acetate, 50% in water)	4.0
	water	38.6

- 15 The portion of the composition that was removed for shelf life testing had not set 2 months later.

Example 8:

A ready mixed setting type joint compound was made as in example 3 but with the following formulation:

		weight %
20	retarder (Gantrez ES-435, 50% in isopropyl	0.8
	alcohol)	
	cellulose ether	0.3
	lime	0.1
	calcium sulphate hemihydrate	27.7
25	perlite	7.2
	limestone	18.9
	wollastonite	2.6

- 15 -

	weight %
binder (ethylene vinyl acetate, 50% in water)	4.1
water	38.4

The portion of the composition that was removed for shelf life testing had not set 1 month later.

5 **Example 9:**

A ready mixed setting type joint compound was made as in example 3 but with the following formulation:

	weight %
retarder (Gantrez ES-435, 50% in isopropyl alcohol)	0.8
10 cellulose ether	0.3
lime	0.1
calcium sulphate hemihydrate	27.7
perlite	7.2
limestone	18.9
15 kaolin	2.6
binder (ethylene vinyl acetate, 50% in water)	4.1
water	38.4

The portion of the composition that was removed for shelf life testing had not set 1 month later.

20 **Example 10:**

A ready mixed setting type joint compound was made as in example 3 but with the following formulation:

	weight %
retarder (Gantrez ES-435, 50% in isopropyl alcohol)	0.8

- 16 -

	weight %
cellulose ether	0.3
lime	0.1
calcium sulphate hemihydrate	27.7
perlite	7.2
5 kaolin	2.6
binder (ethylene vinyl acetate, 50% in water)	4.1
water	38.4

The portion of the composition that was removed for shelf life testing had not set 1 month later.

10 **Example 11:**

A ready mixed setting type joint compound was made as in example 3 but with the following formulation:

	weight %
retarder (Gantrez ES-435, 50% in isopropyl alcohol)	1.0
15 cellulose ether	0.3
lime	0.1
calcium sulphate hemihydrate	35.9
perlite	7.1
limestone	8.1
20 wollastonite	2.6
kaolin	2.6
binder (ethylene vinyl acetate, 50% in water)	4.1
water	38.3

25 The portion of the composition that was removed for shelf life testing had not set 1 month later.

- 17 -

Example 12:

A ready mixed setting type joint compound was made as in example 3 but with the following formulation:

		weight %
	retarder (Gantrez ES-435, 50% in isopropyl	0.7
5	alcohol)	
	cellulose ether	0.3
	lime	1.0
	ordinary Portland cement	27.7
	perlite	6.9
10	limestone	15.8
	wollastonite	2.5
	kaolin	2.5
	binder (ethylene vinyl acetate, 50% in water)	4.0
	water	38.6

- 15 The portion of the composition that was removed for shelf life testing had not set 1 week later.

Example 13:

A ready mixed setting type joint compound was made as in example 3 but with the following formulation:

		weight %
20	retarder (Gantrez ES-435, 50% in isopropyl	0.8
	alcohol)	
	retarder (Narlex D72)	0.03
	cellulose ether	0.3
	lime	0.9
25	calcium sulphate hemihydrate	26.2
	perlite	6.5
	limestone	15.0

- 18 -

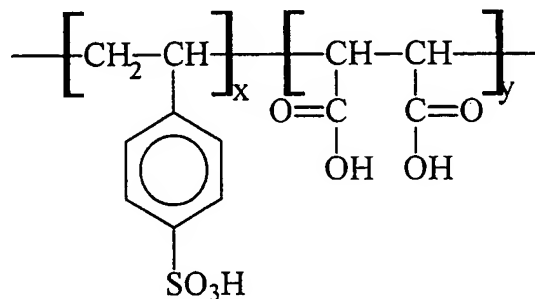
	weight %
wollastonite	2.3
kaolin	2.3
binder (ethylene vinyl acetate, 50% in water)	3.7
water	42.0

- 5 The portion of the composition that was removed for shelf life testing had not set 3 months later.

Setting type ready mixed joint compound compositions according to the invention have been found to have a long shelf life, excellent workability after the accelerator is added until hardening takes place, short setting times so
10 that the length of time required between application of successive coats is reduced compared to drying type joint compounds and are not prone to shrinkage. Compositions according to the invention may also be used as drying type
15 joint compounds if the ready mixed composition is applied without being combined with an accelerator. When compositions according to the invention are used as drying type joint compounds, the drying times are short.

Claims

1. A ready mixed cementitious composition which sets when mixed with an effective amount of a setting accelerator comprising a mixture of: a cementitious material; water; and
 5 a retarder comprising a polymer or a copolymer of a monomer of the formula:



where x and y are integers and may be the same or different or an ionised form thereof.

2. A ready mixed cementitious composition which sets when
 10 mixed with an effective amount of a setting accelerator comprising a mixture of: a cementitious material; water; and a retarder comprising a rosin modified maleic anhydride polymer or copolymer or an ionised form thereof.

3. A composition according to claim 2 in which the polymer
 15 or copolymer is dissolved in isopropyl alcohol.

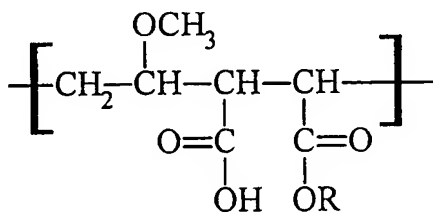
4. A composition according to claim 1, 2 or 3 in which the polymer is present in the composition in an amount of about 0.5% to about 5% by weight of the cementitious material in the composition.

- 20 5. A composition according to any preceding claim in which the polymer is present in the composition in an amount of

- 20 -

about 1.4% by weight of the cementitious material in the composition.

6. A ready-mixed cementitious composition which sets when mixed with an effective amount of a setting accelerator, the composition comprising a mixture of: a cementitious material; water; and a retarder comprising a polymer or copolymer of a monomer having the formula:

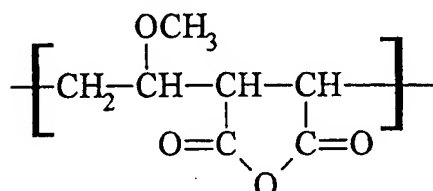


wherein R is C₄H₉ or (CH₃)₂CH or an ionised form thereof.

7. A composition according to claim 6 wherein R is C₄H₉.
8. A composition according to claim 6 or 7 in which the polymer is present in the composition in an amount of about 0.5% to about 5% by weight of the cementitious material in the composition.
9. A composition according to any of claims 6, 7 and 8 in which the polymer is present in the composition in an amount of about 1.4% by weight of the cementitious material in the composition.
10. A composition according to any of claims 6 to 9 in which the polymer or copolymer is dissolved in isopropyl alcohol.
11. A ready mixed cementitious composition which sets when mixed with an effective amount of a setting accelerator, the composition comprising:

- 21 -

a calcium sulphate hemihydrate; water; and a retarder comprising 0.09 to 0.1% by weight plaster of a polymer or copolymer of a monomer having the formula:



5 and having a molecular weight in the range of about 110 000 to about 140 000 or an ionised form thereof.

12. A composition according to any preceding claim having a pH of at least 7.

10 13. A composition according to any preceding claim in which the polymer is present in the composition in an amount of about 0.5% to about 5% by weight of the cementitious material in the composition.

14. A composition according to any preceding claim in which the cementitious material is a calcium sulphate hemihydrate.

15 15. A composition according to claim 14 in which the calcium sulphate hemihydrate is alpha calcium sulphate hemihydrate.

16. A composition according to claim 14 or 15 in which the calcium sulphate hemihydrate is present in the composition
20 in an amount of about 5% to about 50% by weight of the composition.

17. A composition according to any preceding claim in which the calcium sulphate hemihydrate is present in the

- 22 -

composition in an amount of about 30% by weight of the composition.

18. A composition according to any preceding claim further comprising a binder.

5 19. A composition according to claim 18 in which the binder is a polymeric binder and comprises at least one of acrylic, styrene acrylic, styrene butadiene, vinyl acetate and ethylene vinyl acetate.

10 20. A composition according to claim 18 or 19 in which the binder comprises ethylene vinyl acetate.

21. A composition according to claim 18, 19 or 20 in which the binder is present in the composition in an amount of about 1% to about 10% by weight of the composition.

15 22. A composition according to any of claims 18 to 21 in which the binder is present in the composition in an amount of about 1% to about 7% by weight of the composition.

23. A composition according to any of claims 18 to 22 in which the binder is present in the composition in an amount of about 4% by weight of the composition.

20 24. A composition according to any preceding claim further comprising a thickener.

25 25. A composition according to claim 24 in which the thickener comprises at least one of cellulose ether, modified cellulose ether, starch, gum arabic, acrylic, urethane and polyvinyl alcohol.

26. A composition according to any of claims 24 or 25 in which the thickener comprises cellulose ether.

- 23 -

27. A composition according to claim 24, 25 or 26 in which the thickener is present in the composition in an amount of about 0.05% to about 5% by weight of the composition.

5 28. A composition according to any of claims 24 to 27 in which the thickener is present in the composition in an amount of about 0.3% by weight of the composition.

29. A composition according to any preceding claim further comprising a filler.

10 30. A composition according to claim 29 in which the filler comprises at least one of perlite, limestone, celite, dolomite, silica, talc, vermiculite, kaolin, wollastonite, glass microspheres and polymer microspheres.

15 31. A composition according to claim 29 or 30 in which the filler comprises at least one of perlite, limestone and celite.

32. A composition according to claim 30 or 31 in which perlite is present in an amount of no more than 12% by weight of the solids of the composition.

20 33. A composition according to claim 29, 30, 31 or 32 in which the filler is present in the composition in an amount of about 10% to about 20% by weight of the composition.

34. A composition according to any preceding claim further comprising a non levelling agent.

25 35. A composition according to claim 34 in which the non levelling agent comprises at least one of silicas and clays.

36. A composition according to any preceding claim further comprising a preservative.

- 24 -

37. A composition according to claim 36 in which the preservative comprises at least one of formaldehyde and an isothiazolone.

5 38. A composition according to any preceding claim which does not set for at least ten months after formulation.

39. A method of preparing a ready mixed cementitious composition which sets when mixed with an effective amount of a setting accelerator according to any preceding claim comprising mixing together the components of the composition

10 40. A ready mixed coating system comprising separate first and second components, the first component comprising a composition according to any of claims 1 to 38 and the second component comprising a setting accelerator which when mixed with the cementitious composition induces the
15 cementitious composition to set.

41. A system according to claim 40 in which the accelerator comprises at least one of aluminium sulphate, zinc sulphate and iron sulphate.

20 42. A system according to claim 40 or 41 in which the accelerator comprises aluminium sulphate.

43. A system according to claim 40, 41 or 42 in which the accelerator is in the form of a powder.

44. A system according to claim 40, 41 or 42 in which the accelerator is in the form of a paste.

25 45. A system according to claim 40, 41 or 42 in which the accelerator is in an aqueous solution.

- 25 -

46. A system according to any of claims 40 to 45 in which the accelerator is present in the composition in an amount of from about 0.1% to about 5% by weight of the composition.

5 47. A system according to any of claims 40 to 46 in which the accelerator is present in the composition in an amount of about 2% by weight of the composition.

48. A method for preparing a setting coating composition comprising admixing the first and second components of any of claims 40 to 47.

10 49. A method according to claim 48 in which the step of admixing the first and second components comprises:
separately coating the first and second components onto respective surfaces; and
bringing the respective surfaces together so that the first
15 and second components mix at the interface between the components.

50. A ready mixed cementitious composition substantially as described with reference to example 1 or 13.

51. A ready mixed coating system substantially as described
20 with reference to example 2.

52. A ready mixed coating system substantially as described with reference to any of examples 3 to 13.

53. A method for preparing a ready mixed cementitious composition substantially as described with reference to any
25 of the examples.

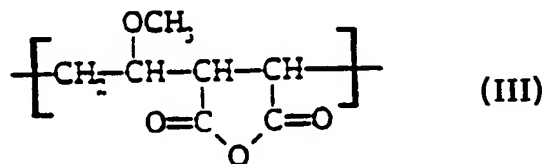
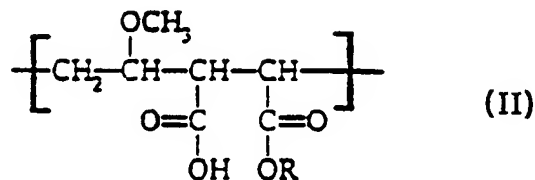
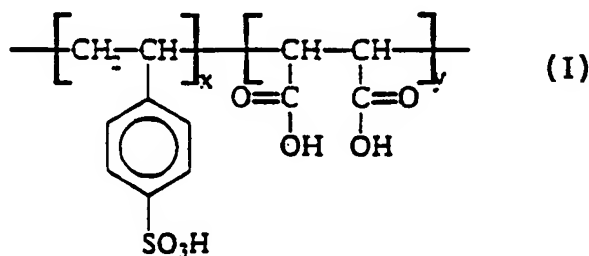
54. A method for preparing a setting coating composition substantially as described with reference to any of the examples.



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C04B 28/02, 28/14, 40/06, 24/26 // (C04B 28/02, 24:16, 40:06), (C04B 28/14, 24:26, 40:06), C04B 103:20		A3	(11) International Publication Number: WO 99/48833
			(43) International Publication Date: 30 September 1999 (30.09.99)
(21) International Application Number: PCT/GB99/00926		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).	
(22) International Filing Date: 24 March 1999 (24.03.99)		Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
(30) Priority Data:			
9806314.2 24 March 1998 (24.03.98) GB			
9812929.9 15 June 1998 (15.06.98) GB			
9821152.7 29 September 1998 (29.09.98) GB			
(71) Applicant (for all designated States except US): BPB PLC [GB/GB]; Langley Park House, Uxbridge, Slough SL3 6DU (GB).			
(72) Inventors; and			
(75) Inventors/Applicants (for US only): O'KEEFE, Samantha, Jane [GB/GB]; 36 Barton Road, Barlestone, Nuneaton, Warks CV13 0EP (GB). FREEGARD, Graham, John [GB/GB]; 3 The Mews, Colston Bassett, Notts NG12 3FB (GB).			
(74) Agent: MARLOW, Nicholas, Simon; Reddie & Grose, 16 Theobalds Road, London WC1X 8PL (GB).		(88) Date of publication of the international search report: 11 November 1999 (11.11.99)	

(54) Title: READY MADE CEMENTITIOUS COMPOSITION



(57) Abstract

The invention provides ready mixed composition comprising: calcium sulphate hemihydrate; water; and a retarder comprising one of the following: (1) a polymer or a copolymer of a monomer of formula (I) (2) a modified maleic anhydride polymer or copolymer. (3) a polymer or copolymer of a monomer having formula (II) wherein R is C₄H₉ or (CH₃)₂CH. (4) 0.09 to 0.1 % by weight plaster of a polymer or copolymer of a monomer having formula (III) and having a molecular weight in the range of about 110 000 to about 140 000. The invention provides ready mixed gypsum plaster jointing compounds with long shelf lives which can be induced to set by the addition of an accelerator. The invention also provides a ready mixed coating system comprising a gypsum composition as described above and a setting accelerator which when mixed with the cementitious composition induces the cementitious composition to set.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakhstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C04B28/02 C04B28/14 C04B40/06 C04B24/26 //(C04B28/02,
24:16,40:06), (C04B28/14,24:26,40:06), C04B103:20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C04B C09J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 076 852 A (BLOYS JAMES B ET AL) 31 December 1991 (1991-12-31) column 4, line 7 - line 28 ---	1,39,40
Y	US 5 653 797 A (PATEL JASHBHAI M) 5 August 1997 (1997-08-05) cited in the application the whole document --- -/--	6-19, 21-32, 34-36, 40-42, 46,53

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

A document defining the general state of the art which is not considered to be of particular relevance

E earlier document but published on or after the international filing date

L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

Z document member of the same patent family

Date of the actual completion of the international search

8 July 1999

Date of mailing of the international search report

14. 09. 99

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Theodoridou, E

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2 790 724 A (W.E.BERGMAN) 30 April 1957 (1957-04-30) column 7, line 13 - line 16 column 9, line 12 - column 10, line 46 column 12, line 65 - line 75 ---	6-19, 21-32, 34-36, 40-42, 46,53
A	DE 33 14 475 A (HENKEL KGAA) 25 October 1984 (1984-10-25) page 2, line 26 - page 3, line 3 page 7, line 7 - line 22 page 8, line 7 - line 30 ---	6-9, 11-14
A	US 3 544 344 A (PRATT RICHARD J ET AL) 1 December 1970 (1970-12-01) the whole document ---	6-8
A	PATENT ABSTRACTS OF JAPAN vol. 095, no. 005, 30 June 1995 (1995-06-30) & JP 07 048158 A (NIPPON ZEON CO LTD), 21 February 1995 (1995-02-21) abstract ---	6,7
A	DE 196 10 270 A (SANDOZ AG) 19 September 1996 (1996-09-19) page 4, line 5 - line 37; example 1 ---	6
A	GB 1 065 081 A (IMPERIAL CHEMICAL INDUSTRIES) the whole document ---	6,11,40, 48,49
A	GB 2 121 811 A (LOCTITE CORP) 4 January 1984 (1984-01-04) claim 22 ---	48,49
A	DE 34 27 741 A (IDEMITSU PETROCHEMICAL CO) 14 February 1985 (1985-02-14) -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 99/00926

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5076852	A	31-12-1991	US 5038863 A	13-08-1991
			CA 2047485 A	21-01-1992
			DE 69114199 D	07-12-1995
			DE 69114199 T	04-04-1996
			EP 0467654 A	22-01-1992
			NO 303982 B	05-10-1998

US 5653797	A	05-08-1997	CA 2196233 A	27-10-1997
			US 5779786 A	14-07-1998

US 2790724	A	30-04-1957	NONE	

DE 3314475	A	25-10-1984	CA 1244181 A	01-11-1988
			EP 0132507 A	13-02-1985
			US 4512808 A	23-04-1985

US 3544344	A	01-12-1970	NONE	

JP 07048158	A	21-02-1995	NONE	

DE 19610270	A	19-09-1996	AT 402921 B	25-09-1997
			AT 49296 A	15-02-1997
			AU 705260 B	20-05-1999
			AU 4807596 A	26-09-1996
			FR 2731699 A	20-09-1996
			GB 2298860 A,B	18-09-1996
			IT RM960172 A	15-09-1997
			JP 8259293 A	08-10-1996
			US 5911819 A	15-06-1999

GB 1065081	A		NONE	

GB 2121811	A	04-01-1984	AU 1549383 A	15-12-1983
			DE 3320918 A	15-12-1983
			FR 2528440 A	16-12-1983
			JP 59004667 A	11-01-1984

DE 3427741	A	14-02-1985	JP 1018028 B	03-04-1989
			JP 1535826 C	21-12-1989
			JP 60033242 A	20-02-1985
			GB 2144730 A,B	13-03-1985
			US 4662942 A	05-05-1987
